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Atmospheric
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Discussions

Interactive comment on "Reformulating atmospheric aerosol thermodynamics and hygroscopic growth into haze and clouds" *by* S. Metzger and J. Lelieveld

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The authors have attempted to develop new techniques/approaches to efficiently solve the multi-phase aerosol equilibrium problem. However, there are several serious issues that must be addressed and clarified before EQSAM3 can be used with any confidence:

1. It is not clear how the calculation of aerosol water content in EQSAM3 is conceptually any different (and more efficient) than what is being done in most aerosol models available in the literature. For example, on page 860, section 3, the authors talk about reformulating the "classical" treatment of equilibrium thermodynamics of atmospheric aerosols into something that consistently treats aerosol

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water. However, their supposedly “new” approach looks exactly like the widely used ZSR method in which single salt molalities $m_{ss}(a_w)$ at a given water activity a_w (with a_w = RH) are used to estimate the total water content. The ZSR equation looks identical to equation (23) derived in this paper (page 869, line 6). The authors eventually admit this on page 871, line 11, but then what is the "new concept” here.

One practical difference is in the way $m_{ss}(a_w)$ is estimated. While most other aerosol models use polynomials for $m_{ss}(a_w)$ in a_w, the authors have derived here a new expression for $m_{ss}(a_w)$ as a function of RH, v_w, and v_e (i.e., equation 20). However, it is not clear if equation (20) is any better than the polynomials in terms of efficiency or accuracy. While equation (20) is valid down to the deliquescence RH (DRH) for a given compound, the accuracy may suffer at lower RH. For example, at 50% RH the equilibrium molality of NaCl is 13.67 mol/kg according to equation (20). This value is about 20% higher than the molality predicted by the comprehensive AIM Model, which is regarded as a benchmark model for aerosol thermodynamic calculations (http://mae.ucdavis.edu/wexler/aim.html/). While this assessment of the overall accuracy of equation (20) is by no means exhaustive, it illustrates an important point that equation (20) gives an approximate value that can have appreciable errors below DRH. This directly affects the calculated aerosol water content, especially in metastable aerosols at low RH. Thus, polynomial fits of the observed molalities as a function of a_w (with a_w = RH) may still be a better choice for higher accuracy over the entire RH range.

In any case, the authors need to clearly contrast the “newness” in their reformulated approach if there is indeed anything substantially different other than the way $m_{ss}(a_w)$ is estimated.

2. A similar argument can be made for the treatment of activity coefficients. While expressing binary activity coefficients as a function of a_w is indeed a rather clever approach, the EQSAM3 model simply assumes that activity coefficients of elec-

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trolytes in a multicomponent mixture equal to binary activity coefficients values as a function of a_w. This is not always a good assumption. Zaveri et al. (2005) clearly showed that multicomponent activity coefficients in representative salt mixtures can be significantly different than the binary values, especially at RH below 80%.

On page 889, line 4, the authors state that Zaveri et al. (2005) applied the activity coefficient methods to laboratory conditions without the required transformation to the atmosphere. This is simply incorrect. Zaveri et al. (2005) evaluated different activity coefficient methods under atmospheric conditions, with water activity a_w = RH. Water content was also computed with the ZSR equation under atmospheric conditions, using single solute molalities evaluated as a function of a_w (with a_w = RH). All this is very clearly stated in the paper.

A more careful analysis is needed than what is presented in Figure 3 to clearly demonstrate the impact of the simplified activity coefficient approach on the overall accuracy of gas-particle partitioning calculations in EQSAM3. The authors need to select a few well-defined test cases and compare the EQSAM3 results with the online AIM model which uses the highly accurate Pitzer-Simonson-Clegg (PSC) module for activity coefficients. ISORROPIA and SCAPE2 use Bromley and/or Kusik and Meissner multicomponent activity coefficient modules, which are not considered as benchmarks for accuracy (as the authors seem to have assumed here).

3. There are several problems in the way solid-liquid partitioning is treated in EQSAM3. First, it is well known that Mutual Deliquescence RH (MDRH) is always lower than individual DRHs of all the salts present in a given multicomponent mixture (e.g., see Wexler and Seinfeld, 1991, Atmos. Environ., 25A, 2731-2748). However, on Page 872, bullet 7, line 20, the authors state that "*... all compounds for which the DRH is below that of the mixed solution are assumed to be precipitated (solid).*" How could this algorithm even work, because the DRHs of

individual salts are never lower than the MDRH of the mixed particle? Also, what is the role of ambient RH in this algorithm?

Second, as described on page 871, line 16, the use of equation (21) to calculate MDRH is questionable. To prove the feasibility of this approach, the authors need to do a direct comparison of MDRHs predicted by equation (21) with those predicted by the AIM online model for several representative mixtures. This is a pretty straightforward exercise that should not take much time or effort.

Third, assuming that EQSAM3 can somehow correctly predict MDRH, then how is the complex multistage growth computed in the mixed-phase region that exists between the MDRH and the complete deliquescence RH (CDRH) without using some sort of an iterative numerical solver (e.g., see discussion in Zaveri et al., 2005b, J. Geophys. Res., 110, D24203, doi:10.1029/2004JD005618)? Does EQSAM3 simply assume that no solid phase exists for any RH above MDRH? If so, then this should be clearly stated. This is an oversimplification that can introduce errors in the calculated aerosol water content for mixed-phase particles. In any case, this certainly should not be viewed as some novel approach to increase model efficiency; any model can make this assumption and become more efficient, but at the cost of accuracy.

If, however, EQSAM3 does solve the solid-liquid equilibrium problem between the MDRH and CDRH, then a direct comparison with the AIM model results is warranted before one can make any claims about the accuracy of EQSAM3. Again, well-defined representative test cases should be selected for model intercomparison before comparing the models using field measurements which have their own uncertainties. It is well known that models such as ISORROPIA and SCAPE2 make some simplifying assumptions (for increased efficiency) when calculating gas-solid-liquid partitioning, which may introduce errors in the solution (e.g., see Ansari and Pandis, 1999, Aerosol Sci. Technol., 331, 129-131.). While it is useful to compare EQSAM3 with ISORROPIA and SCAPE2, they should not be considered as benchmarks for accuracy (as the authors seem to imply on page 890, line 20).

4. It is not at all clear how EQSAM3 analytically and non-iteratively computes multicomponent gas-particle partitioning over size-distributed aerosol particles. Gas-particle partitioning over size-distributed aerosols is a competitive, dynamic process in which aerosol particles of different sizes have different time scales to reach equilibrium with respect to the gas-phase species. EQSAM3 is an equilibrium model, and therefore cannot by itself give an accurate solution for gas-particle partitioning under any RH and size-distributed aerosol composition conditions. A dynamic gas-particle mass-transfer solver is needed to accurately simulate the evolution of aerosol size distribution and composition (especially for semi-volatile species such as HNO_3, HCl, and NH_3). EQSAM3 does not have such a solver.

   The authors do not clearly show any EQSAM3 results for gas-particle partitioning over size-distributed aerosols to prove that their approach works, and nowhere in the paper (the introduction would be appropriate) is the issue of mass-transfer, dynamic models, and limitations of equilibrium models even mentioned.

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